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DERWENT-WEEK: 200161

TITLE: Raw materials for manufacturing **silicon** system membrane for super LSI's comprises silane system compositions containing specified amount of **monochlorosilane**

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PATENT-FAMILY:

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APPLICATION-DATA:

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CIPP	F25 J 3/02 20060101
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ABSTRACTED-PUB-NO: JP 2001064774 A

BASIC-ABSTRACT:

NOVELTY - A raw material for manufacturing **silicon** system membrane comprises silane system compositions containing not less than 10 weight ppm of **monochlorosilane**.

USE - Used as the raw material of **silicon** system membrane applicable to super LSI's, photoelectromotive elements, and membrane transistors.

ADVANTAGE - Using this raw material **silicon** system membrane can be synthesized with higher rate than those of conventional methods without reducing the characteristics of the product, besides super purifying processes as in the conventional plants using super purity **monosilane** or halogenated silane becomes unnecessary.

EQUIVALENT-ABSTRACTS:

A glass substrate in a evacuated reaction chamber of CVD device was heated by a heater which has been buried in its holder up to 200 degreesC then **monosilane** gas containing 200 ppm of **monochlorosilane** was introduced into the chamber at the rate of 20 ml/(minute) so that the inner pressure of the chamber to be 80 mTorr then high frequency (20 W) was applied on electrodes to deposit amorphous membrane (thickness 1 micron) on the substrate.

TITLE-TERMS: RAW MATERIAL MANUFACTURE **SILICON** SYSTEM MEMBRANE SUPER COMPRISE SILANE COMPOSITION CONTAIN SPECIFIED AMOUNT

DERWENT-CLASS: **E36** L03 Q75 U11 U12 U13

CPI-CODES: E31-P06A; E31-P06B; L04-C; L04-E; L04-F;

EPI-CODES: U11-C18A1; U12-B03A; U12-B03C; U13-C06;

CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation Code B114 B720 B751 B760 B831 C017 C100 C101 C800 C804 C805 C806 C807 M411 M730 Q452 Q454 Specific Compounds RA08HC Registry Numbers 211573

Chemical Indexing M3 *02* Fragmentation Code B114 B720 B760 B831 C101 C800 C802 C804 C805 C806 C807 M411 M730 Q452 Q454 Specific Compounds R01831 Registry Numbers 3801

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(54) RAW MATERIAL FOR PRODUCING SILICON SERIES THIN FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To eliminate the need of gas mixing operation in the use and to simplify a refining stage at the time of production by allowing monochlorosilane by an amt. equal to or above the specified amt. to be contained in a silane series compsn.
SOLUTION: This raw material for producing a silicon series thin film is composed of a silane series compsn. contg. monochlorosilane of ≥10 ppm by a weight standard. The silane series compsn. may contain the other silanes such as a silane halide and monosilane, but, desirably, it contains monosilane of the amt. by which the molar ration between it and monocholorosilane is controlled to 1:99 to 95:5. By using such raw material, by a plasma CVD method, a silicon series thin film is produced. The amorphous silicon film in which residual chlorine content is controlled to 0.005 to 5 atomic % and exhibiting excellent photodeterrioration resistance and sufficient photoelectric characteristics and easily and stably be obtd. at a high speed. The raw material can be produced by distilling the one obtd. by subjecting silane chloride hydride to disproportionation.

CLAIMS

[Claim(s)]

[Claim 1]A raw material for silicon system thin film fabrication which consists of a Silang system constituent which contains a not less than 10 ppm monochloro silane by a weight reference.

[Claim 2]The Silang system constituent which contains a not less than 10 ppm monochloro silane by a weight reference, The raw material for silicon system thin film fabrication according to claim 1, wherein it is the Silang system constituent containing a mono silane and a monochloro silane and a mole ratio of a mono silane and a monochloro silane which are contained in this constituent is the Silang system constituent which are 1:99-99:1.

[Claim 3]A formation method of a silicon system thin film using the raw material for silicon system thin film fabrication according to claim 1 or 2 as a silicon raw material in a method of manufacturing a silicon system thin film with plasma CVD method.

[Claim 4]A manufacturing method of the raw material for silicon system thin film fabrication according to claim 1 or 2 distilling a reaction constituent obtained by carrying out disproportionation of chlorination hydrogenation Silang.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the raw material used for manufacture of the silicon system thin film used for very large scale integration, a photovoltaic cell, a thin film transistor, etc.

[0002]

[Description of the Prior Art]Conventionally, in order to satisfy the demand to high reliability and highly efficient characteristic for manufacture of the silicon system thin film used for electron devices, such as very large scale integration, a photovoltaic cell, and a thin film transistor, it is common to it that the monosilane gas of super high purity is used as the raw material. By using super-high-purity monosilane gas, it is possible for the semiconductor membrane of a silicon system with few defects originating in an impurity to be formed, and to, manufacture a highly efficient electron device with sufficient reproducibility as a result.

[0003]As a general manufacturing method of monosilane gas, for example to JP,64-3806,B. As a method of manufacturing in large quantities, Silang useful as basic materials of high purity silicon (high grade polycrystalline silicon used as a high grade single crystal silicon wafer or its raw material), Hydrogenation chlorination silicon (halogenation Silang) used as a raw material is supplied to the reactor which has a distillation function, it disproportions under existence of a catalyst, and manufacturing continuously the silane compound whose hydrogenation rate which uses a mono silane as the main ingredients is higher than the upper part of a reactor is shown.

[0004]According to JP,06-174364,A, about the manufacturing method of the monosilane gas of super high purity, the method of extracting the super-high-purity monosilane gas refined while introducing into a rectifying tower the monosilane gas manufactured, for example by the above methods and refluxing it is indicated. And according to this method, it is shown that the monosilane gas and the mono-silane fluid of super high purity which have the purity beyond 99.9999wt% can manufacture continuously.

[0005]By the way, as a method for manufacturing a reliable electron device, not only the method of only high-grade-izing material gas but the following approaches are tried actually. Namely, only the purity of a thing with the feature that generation of the defect which surely originates in an impurity is low controlled when a high grade raw material is used, and monosilane gas does not determine device performance, It is generally reported that improvement in device performance is realizable also by technical improvement on device fabrication.

[0006]As the example, the art which forms an amorphous silicon film by introducing the silicon

compound gas containing a fluorine atom into the plasma formed of a electron cyclotron resonance is indicated by JP,8-1896,B. While being able to make a film deposit at high speed according to this art, without generating the granular material (powder) leading to membranous structural failure, it is supposed that it is possible to form the film which has the Takamitsu conductivity also in a room temperature.

[0007]To JP,2-34863,A, SiF_4, $SiCl_4$, The method of forming the electro photography photo conductor which comprises an amorphous silicon film by a electron cyclotron resonance method using the silicon compound containing halogen, such as SiH_2Cl_2 and $SiHCl_3$, is indicated. the case where more than 40atomic% is used as a total amount of the hydrogen contained in a film, and a halogen atom at this time -- powder -- generating **** -- it is supposed that the amorphous silicon film which is excellent in an electrifying characteristic without things at high speed can be formed.

[0008]Applied Physics Monosilane gas and dichloro silane gas are mixed on a letter {Applied Physics Letter 65 (1994) and p1949}, It is shown that an amorphous silicon film can be produced at high speed, without generating powder by using a direct-current-discharge CVD method.

[0009]

[Problem(s) to be Solved by the Invention]Thus, the use of super-high-purity monosilane gas can suppress the defective formation originating in an impurity low, when manufacturing various electron devices, but. In order to manufacture a more highly efficient silicon system thin film, it is supposed that it is effective in material gas to add halogenation silane gas. However, according to this invention person's etc. examination, it became clear that there is a problem as follows at this time.

[0010]Namely, when mixing and using monosilane gas and halogenation silane gas, usually supply into a reaction vessel independently, without making each gas stored in the cylinder etc. join beforehand within piping, or making it join, but. If gas is not uniformly mixed at this time, the performance of the silicon system thin film obtained and by extension, an electron device may show dispersion.

[0011]Since each of each material gas mixed is the super-high-purity articles which passed through the advanced purification process, the actual condition is being unable to say that it is efficient in the field of the productivity at the time of manufacturing each gas.

[0012]This invention persons did not need the operation which mixes especially gas as a raw material at the time of manufacturing the silicon system thin film used for an electron device etc. in view of such the actual condition, but made it the technical problem to provide the ideal raw material which can be simplified substantially for a purification process on the occasion of the manufacture moreover.

[0013]

[Means for Solving the Problem]This invention persons inquired wholeheartedly that an aforementioned problem should be solved. As a result, in a high grade mono silane as a semiconductor raw material, it is considered an impurity, And if monosilane gas containing a monochloro silane by which it is made difficult to store in containers, such as a cylinder, generally is led to a direct reaction container etc. and a silicon system thin film is manufactured with plasma CVD method, knowledge that a good silicon system thin film can be manufactured will be acquired, and it came to complete this invention.

[0014]That is, this invention is a raw material for silicon system thin film fabrication which consists of a Silang system constituent which contains a not less than 10 ppm monochloro silane by a weight reference. If it puts in another way, it will be use as a raw material for silicon system thin film fabrication of the Silang system constituent which contains a not less than 10 ppm monochloro silane by a weight reference.

[0015]The Silang system constituent which constitutes a raw material for silicon system thin film fabrication of above-mentioned this invention, especially this raw material for silicon system thin film fabrication, It is the Silang system constituent containing a mono silane and a monochloro silane, A mole ratio of a mono silane and a monochloro silane which are contained in this constituent a raw material for silicon system thin film fabrication which are 1:99-99:1, and the Silang system constituent that is especially 5:95-95:5, For example, it can be conveniently used as a silicon raw material at the time of manufacturing a silicon system thin film with plasma CVD method.

[0016]In a way other this inventions manufacture a silicon system thin film with plasma CVD method, Are it a formation method of a silicon system thin film by which it is characterized to use a raw material for silicon system thin film fabrication of said this invention as a silicon raw material, and this invention of further others, It is a manufacturing method of a raw material for silicon system thin film fabrication of said this invention distilling a reaction constituent obtained by carrying out disproportionation of chlorination hydrogenation Silang.

[0017]As described above, a monochloro silane is considered to be an impurity of a mono silane as a raw material for silicon system thin film fabrication, equivalent to the Silang system constituent which constitutes a raw material for silicon system thin film fabrication of this invention from a process in which a high grade mono silane is manufactured, after disproportioning chlorination hydrogenation Silang -- {-- that is, Though} rough generation article which contains a monochloro silane more than 10 ppm (wt.) was obtained, An example which uses this rough generation article, especially the Silang system constituent contained by high concentration which monochloro silane concentration says more than 1wt% (further 5wt% more than or 10wt% more than) as a raw material for silicon system thin film fabrication as it was does not exist, as far as this invention person etc. get to know.

[0018]It is shown that the above rough generation articles can use this invention as a raw

material for silicon system thin film fabrication, If an abbreviation of a purification process which requires great cost and time and effort was possible, when it not only closed, but a raw material for silicon system thin film fabrication of this invention is manufactured, for example with a manufacturing method of above-mentioned this invention, If possible, it closes obtaining without including a destabilizing factor of mixing operation for a merit by concomitant use with the halogenation Silang.

[0019]

[Embodiment of the Invention]The raw material for silicon system thin film fabrication of this invention consists of a Silang system constituent which contains not less than 10 ppm of monochloro silane gas by a weight reference at least. It is a weight reference altogether also about the following ppm displays.

[0020]When a mono- KURORU silane is not contained in the Silang system constituent, and when [though the monochloro silane was contained,] the concentration is less than 10 ppm, When forming a silicone film on condition of usual with a CVD method, it is generated by powder in plasma and becomes a cause of the degradation of the element to manufacture, and a fall of a manufacturing yield. When it is going to obtain a quality film, without making powder generate, it must stop having to reduce a film deposition rate remarkably. Not less than 10 ppm of especially suitable monochloro silane concentration is not less than 50 ppm rather than being able to set from such a viewpoint in the raw material for silicon system thin film fabrication of this invention. As concentration of the viewpoint referred to as not needing manufacturing MERRITO mentioned later, i.e., an advanced purification process, to a monochloro silane, it is preferred more than 1wt% and also more than 5wt%, and that it is more than 10wt% especially.

[0021]The raw material for silicon system thin film fabrication of this invention will not be limited especially if it consists of a Silang system constituent which contains not less than 10 ppm of monochloro silane gas at least, In the range which does not have an adverse effect when it is used for this Silang system constituent as a silicon source at the time of forming a silicon system thin film with plasma CVD method (only henceforth a film production material raw material). Reducing gas, such as hydrogen; other ingredients, such as other Silang;, such as other halogenation Silang; mono silanes, such as inactive gas; dichloro silanes, such as nitrogen and argon, and trichlorosilan, a disilane, and trishiran, may contain.

[0022]Although the content in particular of an ingredient besides these is not limited, when it is used, it is preferred that a membranous deposition rate contains hydrogenation Silang from a viewpoint of improving remarkably and not being generated by powder at the time of a deposit. To the above-mentioned Silang system constituent, from viewpoints of film production nature when it is especially used with a film production raw material, the quality of the silicon system film obtained, the ease of constituent manufacture, etc. It is preferred that the mole ratio of a

mono silane and a mono- KURORU silane is contained for the mono silane in 1:99-99:1, and quantity that is set especially to 5:95-95:5. Also in the suitable Silang system constituent concerned, other ingredients, such as the same reducing gas as the above, inactive gas, other halogenation Silang, and other Silang, may be contained.

[0023]The depressor effect of above improvement in the speed of film production speed and powder generating is acquired also when hydrogenation Silang and halogenation Silang other than monochloro silanes, such as tetrachlorosilicane, trichlorosilane, and dichlorosilane, are used together, but. Since especially a monochloro silane has high reactivity, it can make quicker the deposition rate of a silicon system thin film. It is also possible to reduce the halogen concentration which remains in a film, since a monochloro silane has few chlorine atoms which itself has than other above halogenation Silang, and it is also possible to reduce the adverse effect which a halogen residual has on an element.

[0024]The state in particular of the Silang system constituent which is a raw material for silicon system thin film fabrication of this invention may not be limited, may be a gas, or may be liquefied, and may be in the state where both live together. In using the raw material for silicon system thin film fabrication of this invention, When the above-mentioned constituent is a gas, liquefied as it is again or since what is necessary is just to introduce into the system of reaction after only gasifying, when it is a vapor-liquid jumble system and it is not accompanied by mixing operation, uneven-ization of the atmosphere within the system of reaction can be prevented.

[0025]Although the monochloro silane is generally structurally unstable and it is made difficult to store in containers, such as a cylinder, about the raw material for silicon system thin film fabrication of this invention obtained by the manufacturing method of above mentioned this invention, for example, it can be used for a direct reaction container etc., leading. If a use stage is managed, it is also possible to use it by the method of being filled up with the Silang system constituent of the presentation which foresaw the amount of decomposition of the monochloro silane, filling up a cylinder. When it mixes with a mono silane etc. and is filled up into a cylinder, the substance with which it is filled up in consideration of the steam pressure of the substance with which it is filled up is in the same state, and all the substances are possible also for a gas or it being altogether liquefied and being filled up, for example.

[0026]When a silicon system thin film is manufactured depending on the method of plasma CVD which is indicated by JP,6-326043,A using the raw material for silicon system thin film fabrication of this invention, Residual chlorinity can be easily high-speed, and is stabilized, and can obtain the amorphous silicon film in which 0.005 - pentatomic %, the outstanding photodegradation-proof characteristic more preferably controlled between 0.01-1 atom %, and sufficient photoelectrical characteristic are shown.

[0027]In the case where the raw material for silicon system thin film fabrication of this invention

is used, As plasma CVD, plasma CVD method with publicly known capacitive coupling type plasma CVD method, inductive-coupling type plasma CVD method, electron cyclotron plasma CVD method, microwave CVD method, ultrashort-waves plasma CVD method, etc. can adopt that there is no restriction in any way. What is necessary is for the film production conditions by the conventional plasma CVD method and the changing point in particular not to have film production conditions, either, and just to determine them suitably according to the plasma generation method etc. which are material-gas-composed or are adopted.

[0028]Although the method in particular of manufacturing the raw material for silicon system thin film fabrication of this invention is not limited, it can be suitably manufactured by the following methods.

[0029]That is, it can manufacture suitably by distilling the reaction constituent obtained by carrying out disproportionation of chlorination hydrogenation Silang.

[0030]Here, the disproportionation of chlorination hydrogenation halogenation Silang is a reaction which makes the silane compound in which chlorination hydrogenation halogenation Silang of a raw material differs, respectively generate by exchanging hydrogen and halogen between the molecules of this chlorination hydrogenation halogenation Silang. Since the compound generated newly repeats the still more nearly same exchange reaction, the system of reaction serves as mixture composition which consists of several kinds of silane compounds.

[0031]As an example, the disproportionation of trichlorosilane is explained below. Under existence of a catalyst, first, trichlorosilanes exchange hydrogen and each other's chlorine and they generate dichlorosilane and tetrachlorosilane as follows. Since dichlorosilane generates a monochloro silane and trichlorosilane similarly and a monochloro silane generates a mono silane and dichlorosilane similarly as shown below, As a result of repeating these reactions, the system of reaction serves as a mono silane, a monochloro silane, dichlorosilane, trichlorosilane, and mixture composition that consists of five ingredients of tetrachlorosilane.

[0032]

[Formula 1]

$$2SiHCl_3 \Leftrightarrow SiH_2Cl_2 + SiCl_4$$

$$2SiH_2Cl_2 \Leftrightarrow SiH_3Cl + SiHCl_3$$

$$2SiHCl_3 \Leftrightarrow SiH_4 + SiH_2Cl_2$$

[0033]Thus, the constituent of a desired presentation can be obtained by adjusting distillation conditions suitably and distilling the obtained mixed composition.

[0034]The trichlorosilane used as the raw material of the above-mentioned disproportionation can be obtained with about about 70 to 90% of yield by making metal silicon and hydrogen chloride gas react at about 300-400 **. Although it is not limited but can apply a publicly known method, since especially the method of disproportioning trichlorosilane can perform

disproportionation and distillation simultaneously, a method which is indicated to above mentioned JP,64-3806,B is preferred for it.

[0035]For example, in the above-mentioned gazette, a catalyst which consists of the 3rd class aliphatic hydrocarbon substitution amine and its hydrochloride is used as a catalyst, Trichlorosilane is supplied from near the Nakagami stage of a reactor which served as a distillation column where a condenser cooled at -60 ** in the upper part, a boiler which a catalyst was beforehand introduced into the lower part and was heated by 130 **, and a catalyst separation tub were connected, By reacting under application of pressure of 2 kg/cm^2, making the downstream reactor upper part circulate through a catalyst in a reboiler from a condenser via a catalyst separation tub, The Silang system constituent which consists of dichlorosilane 6.5% has been obtained monochloro silane 8.5% mono-silane 85% as a condensate of low-boiling point gas which passed the above-mentioned condenser. Thus, when performing disproportionation using a reaction apparatus with a distillation column, that presentation can be easily changed by changing suitably a number of stages and a reflux ratio of a distillation column.

[0036]In a manufacturing method of this invention, a constituent produced by carrying out in this way may be distilled further separately. However, since a raw material for silicon system thin film fabrication of this invention may contain not less than 10 ppm of monochloro silanes, even when distilling further, it does not need to perform rectification like [when obtaining the conventional super-high-purity mono silane].

[0037]

[Example]Although an example and a comparative example are given and this invention is explained concretely hereafter, this invention is not limited to these examples. In this example, the silicon thin film was produced using the plasma CVD device shown in drawing 1.

[0038]The glass substrate was heated at 200 ** by setting the one glass substrate 5 (cm [5] x 5 cmx0.5mmt) on the substrate holder 3 in the capacitive coupled plasma CVD system by which example 1 evacuation was carried out, and energizing to the heater 6 currently embedded in the substrate holder. And it adjusted with the regulation-of-pressure device 8 so that the monosilane gas having contained about 200 ppm (wt.) of monochloro silanes might be supplied by 20-cc the flow for /and the pressure in a reaction vessel might serve as 80mTorr with the gas flow rate controller 11 into a reaction vessel. By impressing the high frequency of the intensity of 20W to the high frequency impression electrode 2 in this state, reaction gaseous plasma was generated and an about 1-micrometer amorphous silicon film was obtained on the substrate. Although reaction time was 55 minutes at this time, the powder-like thing was not observed in plasma. When the characteristic of the obtained film, i.e., the chlorine content in a film, the photodegradation-proof characteristic, and photosensitivity were measured like the method indicated to JP,6-326043,A, each measured value was 0.08atom%,

0.4 time of an initial value, and $4x10^{6}$, respectively.

[0039]The above-mentioned silane system gas (monosilane gas containing 200 ppm of monochloro silanes) used for film production, Dichlorosilane is disproportioned under the catalyst of an amine system (reaction temperature: 50 **, reaction pressure:2.3MPa), and is obtained from the generated chlorosilicane constituent using a distillation column (theoretical plate number: 42 steps, distillation pressure:2.3MPa).

[0040]lowering a reflux ratio in manufacture of the silane system gas in example 2 Example 1 -- a monochloro silane -- 2wt% -- the monosilane gas to contain was manufactured. An about 1-micrometer amorphous silicon film was formed on the glass substrate 5 like Example 1 using this obtained silane system gas. The reaction time required at this time is 40 minutes, and was able to be produced in time shorter than Example 1 (at namely, high speed). The powder-like thing was not observed in the plasma at the time of film production.

[0041]When the physical properties of the obtained film were measured like Example 1, a chlorine content, the photodegradation-proof characteristic, and photosensitivity were 0.1atom%, 0.45 time of an initial value, and $2x10^{6}$, respectively.

The silicone film was deposited on the same conditions as Example 1 except [all] changing material gas into the monosilane gas (made by Nippon Sanso Corp.) which has the purity of 99.9995wt.% in comparative example 1 Example 1. As a result, a 1-micrometer silicon thin film was obtained at the reaction of 3 hours. At this time, a lot of impalpable powder adhered to the view port of the reaction vessel side. Existence of a pinhole was checked when viewing estimated the obtained film.

[0042]

[Effect of the Invention]When the raw material for silicon system thin film fabrication of this invention is used as gas for manufacture, such as very large scale integration, a photovoltaic cell, and a thin film transistor, it becomes possible to manufacture a silicon system thin film at a quick speed, without reducing device performance. When a photovoltaic cell is formed especially, the silicon thin film which is excellent in photodegradation-proof performance can manufacture at high speed.

[0043]Since the raw material for silicon system thin film fabrication of this invention does not include a rectification process in the manufacturing process unlike the mixed composition of the super-high-purity mono silane which is the conventional raw material for silicon system thin film fabrication, or this and other high grade halogenation Silang, its merit is large in respect of manufacturing efficiency or cost.

[Translation done.]